doubt, a long hydrocarbon chain tends both to diminish solubility and to cause the molecules to adhere together on the surface. My experiments have shown a certain amount of independence between the tendency to dissolve and to separate laterally on the surface. Thus films of palmitic acid remain practically insoluble for some 20° above the temperature of expansion, but with cetyl alcohol, the solubility is marked some distance below the temperature of expansion.

It does not seem legitimate to state, *a priori*, what will be the relation between the tendency to dissolve and the tendency to expand; but as both these quantities are now capable of independent measurement, I hope to obtain some results on this problem in the near future.

Diffusion and Intertraction.

By C. G. SCHONEBOOM.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received May 24, 1922.)

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The starting-point of this investigation was the phenomenon which Sir Almroth Wright described in the 'Proceedings of the Royal Society,' Series B, vol. 92. The original experiment is conducted by putting 5 or 8 per cent. NaCl in a test-tube or flat glass cell and allowing some blood serum to run slowly on the top of the NaCl. As soon as the fluids are brought into contact, a mass movement is started, the upper fluid being carried down into the lower and the lower into the upper. The characteristic appearances so produced are well described by the terms intertraction or pseudopodial interpenetration. By colouring the serum with a trace of some dyestuff (*e.g.*, eosin) the intertraction phenomenon is easier to follow; or by having a layer of tannic acid or sulpho-salicylic acid in NaCl solution on the bottom, one sees after a short time (some minutes) a heavy precipitate in the lower interface.

This system, serum on NaCl solution, presents a typical example of the intertraction phenomenon, as will be described in the following experiments, in so far that in the case of serum and NaCl solution both fluids are, so to speak, active and penetrate each other quickly, so that after some time (10 to 30 minutes) the contents of the vessel are a homogeneous mixture, as can readily be seen if eosin be used in the serum. This result, the homogeneous mixing, is completed by ordinary diffusion, which very soon sets in after the intertraction has begun, from the numerous streams and droplets of the serum which come down in the NaCl solution.

One suggestion put forward was that the cause was a water-drawing action by the salt. This view might appear to be supported by Nägeli's suggestion that the colloid particles possess a watery envelope (partly bound chemically as hydrate water and partly as adsorption water).

In view of the above, I started the investigation of various colloids: egg albumen, blood serum, gelatin, gum arabic, tannic acid, and starch. All these give a typical intertraction phenomenon and seem to give support to the suggestion that the salt would abstract water from the colloid, and thus increasing the weight, induce the intertraction.

At the outset I found that for producing intertraction it was not necessary to use salt (NaCl) or other electrolyte. Organic compounds such as urea, chloral hydrate, thiosiamin, phenozason, and acids such as oxalic, citric, tartaric, etc., also produced intertraction with colloids.

An experiment showing this is set forth in Table (Diagram) I below. The fact that electrolytes were not essential to the production of intertraction makes it possible to produce this phenomenon with inorganic colloids also, such as Prussian blue, and with aniline dyes, which are precipitated by concentrated solutions of electrolytes.

Table (Diagram) I.—Gum Arabic Solutions superposed on Quinine Hydrochlorate (Acid Salt) solutions.

Gum arabic percentages.							
25					↓	30	60
18·75					30	60	120
12·5				↓	30	60	
6·25			↓	30	60		
3		↓	45		500		
1·5		45	60	180			
	0·	3	6·25	12·5	25	37·5	50

Quinine percentages.

↓ indicates that the upper solution is heavier and comes down directly by gravity. The figures 30, 60, etc., represent the number of seconds which elapse between the superposition of the gum arabic solution and the starting of pseudopodial intertraction.

The further point then emerged that intertraction phenomena are obtained not only with colloidal solutions, but also with *all* inorganic and organic compounds without any exception, provided always that the substances in question are sufficiently soluble in water and that there is not too great a difference in specific gravity between the upper and lower solutions.

Table (Diagram) II gives an example, taken at random, of the wide range in concentration with which the intertraction phenomenon occurs. In point of fact, solutions of all chemicals (provided they do not react chemically) are found to give approximately the same picture when set out graphically, differing only in the range of concentrations in which the intertraction occurs.

Table (Diagram) II.—HCl 0·1 mol.–2 mols. on KNO_3 0·1 mol.–1 mol.

mol.										
2					strong position. ↓	+	+	+	+	strong position. +
1·9					+	+	+	+	+	+
1·8					+	+	+	+	+	+
1·7					+	+	+	+	+	+
1·6				↓	+	+	+	+	+	+
1·5				+	+	+	+	+	+	+
1·4				+	+	+	+	+	+	+
1·3				+	+	+	+	+	+	+
1·2			↓	+	+	+	+	+	+	+
1·1			+	+	+	+	+	+	+	+
HCl 1			+	+	+	+	+	+	+	+
0·9			+	+	+	+	+	+	+	+
0·8		↓	+	+	+	+	+	+	+	+
0·7		+	+	+	+	+	+	+	+	+
0·6		+	+	+	+	+	+	+	+	+
0·5		+	+	+	+	+	+	+	+	+
0·4	↓	+	+	+	+	+	+	+	+	+
0·3	+	+	+	+	+	+	+	+	+	+
0·2	+	+	+	+	+	+	+	+	+	+
0·1	+	+	+	+	+	+	+			
0										
	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1 m.

KNO_3.

↓ indicates that the upper fluid is heavier and comes down direct by gravity.
+ indicates intertraction.

The next question which presented itself was whether the size of the molecule exerts any effect on the phenomenon. Here I employed both aniline dyes and alkaloids and simple inorganic and organic substances. Experiments showed that the size of the molecules has no influence.

In connection with the suggestion that the intertraction phenomenon might depend on the withdrawing of water, I paid special attention to the varying amount of hydrate water, which is supposed to be weakly held by most salts, bases, and acids, specially in dilute solutions (hydrate theory of Harry Jones and others). For example, salts like disodium phosphate, with a maximum of about 325 hydrate water molecules round them, gave the intertraction phenomenon as well as those which, like the simple potassium salts, are supposed to collect no, or very little, hydrate water round their molecules or ions.

The presence, or absence, of hydrate water, was found to be without any influence on the intertraction phenomenon. The same thing was found to hold true with organic compounds investigated from this point of view. Intertraction is obtained both with glucose, lactose, tartaric acid, citric acid (substances which have little or no hydrate water), and with fructose and cane sugar (substances which have much hydrate water). But in one of the earlier experiments the dehydration was very conspicuous in connection with intertraction. In the experiment in question, cobalt chloride solution (2–2·5 molar) was superposed upon a saturated calcium chloride solution. Here after a short interval (from a few seconds to 1 or 2 minutes), *blue* streams and droplets come down from the *red* cobalt solution into the calcium chloride solution, the change of colour being due to a conversion of the cobalt chloride + $6H_2O$ into the cobalt chloride + $1H_2O$. It was, however, established by taking weaker solutions of the calcium chloride and the cobalt chloride that the intertraction phenomenon occurred also, and to an equal extent, without any colour change, so that the dehydration obtained in strong solutions stands in no causal connection with the intertraction phenomenon.

Final and conclusive evidence that intertraction has nothing to do with dehydration, and occurs quite independently of it, was furnished by the fact that intertraction is also obtained when, instead of water, organic solvents (such as glacial acetic acid, ethyl acetate, amyl acetate, glycerol, amyl alcohol, aniline, pyridine) are employed. Reflection will show that the only forces which can come into operation are forces of surface tension.

Two observations, in particular, seemed to point clearly in that direction. The first was made in the course of an experiment which must here be described in detail. It consists in taking a double series (A and B) of ten test-tubes with graduated sodium chloride solutions, ranging from 0·90 molar, 0·91, 0·92, etc., to 1 molar sodium chloride, and adding to the tubes of series B some drops of a solution of eosin in water, having the same specific weight as the sodium chloride solutions. Then the *coloured* sodium chloride solutions are superposed on the uncoloured solutions, in such a way that the 0·9 coloured solution is put on the 0·91, or 0·92, uncoloured solution, and so on in series; the coloured solutions will then be seen to go down almost immediately after the fashion which I have called pseudopodial intertraction.

When the conditions are varied and the coloured 0·9 solution is placed on the 0·95, or any denser uncoloured solution, intertraction is suppressed, because the forces engaged in intertraction are, in this case, unable to overcome the effect of the larger difference in specific gravity.

The second observation relates to colloidal gold and silver solutions superposed on solutions of urea (varying from 0·5–5 per cent.). When such experiments are carried out, it is found that intertraction is obtained with colloidal solutions which are prepared by chemical means, but the phenomenon fails to occur with solutions prepared by the electric method (direct current arc).

The point of these two experiments is, that the eosin employed in the first experiment is a powerful depressor of surface tension, and in the second experiment, where we are dealing with chemically prepared colloidal gold and silver solutions, we have traces of salts (gold chloride, potassium carbonate, etc.), and organic substances (tannic acid, alcohol, formaldehyde), which alter the surface tension, while in the case of the electrically prepared solutions we have the colloidal particles suspended in pure water (possible traces of oxides can be left out of consideration).

The view that intertraction is dependent on certain relations of surface tension is strongly supported by a passage in an article by Clerk Maxwell on "Capillarity," in the 'Encyclopædia Britannica,' 11th edition, p. 259. This passage, here cited in the form in which it appears in his collected papers, runs as follows:—

"If this quantity (the interfacial tension) is positive, the surface of contact will tend to contract, and the liquids will remain distinct. If, however, it (the interfacial tension) were negative, the displacement of the liquids, which tends to enlarge the surface of contact, would be aided by the molecular forces, so that the liquids, if not kept separate by gravity, would at length become thoroughly mixed.

"No instance, however, of a phenomenon of this kind has been discovered, for those liquids, which mix of themselves, do so by the process of diffusion, which is a molecular motion, and not by the spontaneous puckering and replication of the bounding surface as would be the case if T [the interfacial tension] were negative."

It is of singular interest to find the phenomenon of intertraction here predicted and quite accurately described in advance. Anyone who has observed intertraction will acknowledge that we have, in the above description, an accurate word picture of this phenomenon. After a few seconds one sees the puckering beginning, and in many cases the surface layer of the active fluid is replicated. This is the phenomenon which Sir Almroth Wright called "pseudopodial intertraction."

In addition to this typical intertraction there is another form of mixing—"simple intertraction," which is intermediate between pseudopodial intertraction and the well-known slow processes of diffusion.

Simple intertraction occurs when the difference of the specific gravity of the two superposed fluid layers is greater, and also when the relations of the surface tensions are different from those under which the pseudopodial intertraction happens. There is a gradual transition between pseudopodial intertraction, simple intertraction, and diffusion, as is illustrated in the following experiments:—

A series of long test-tubes (surrounded by a water mantle to eliminate convection movements, caused by temperature differences) are filled to the same height with hydrochloric acid (1 molar). On the hydrochloric acid we superpose in the first tube water, and then, in their order, sodium chloride solutions of the following strengths: 0·001, 0·01, 0·02, 0·04, 0·06, 0·08, 0·1, 0·2, 0·3, and 0·4 molar. To these solutions is added a trace of methyl orange, to act as an indicator of the progress of the acid.

It is now found that in the—

0·4 mol.	NaCl,	the HCl rises	60 mm. in 1 minute	Advancing in the form of pseudopodial intertraction.
0·3	„	„	60 mm. in 12 minutes	
0·2	”	”	progressively slower	Advancing on a level front by what has been called above interpenetration by simple intertraction.
0·1	”	”	” ”	
0·08	”	”	” ”	
0·06	”	”	” ”	
0·04	”	”	” ”	
0·02	”	”	” ”	
0·01	„	„	40 mm. in 12 hours.	
0·001	”	”	39 ” ”	
Water,		the HCl rises	36 mm. in 12 hours.	

We see from the above Table that hydrochloric acid rises in the tubes which contain the weakest salt solutions practically at the same rate as in pure water. Here the dividing line between the red and yellow colour stands after 12 hours about 40 mm. above the base line. In the stronger solutions (*e.g.*, in the 0·1 molar sodium chloride) the hydrochloric acid has risen to the top—in 12 hours more than 200 mm.*

The general results such as those in the experiments above are obtained also with the various acids and bases and with the numerous salts which were investigated. While it holds true that these three forms of mixing (that is diffusion, simple intertraction, and pseudopodial intertraction) are obtained with all substances, it is to be noted that the range of concentrations which give the simple and pseudopodial intertraction is very narrow in some combinations, in others it is extremely wide.

For example, we take a series of sixteen test-tubes and fill them with sodium chloride solutions in progressive concentrations, ranging from 0·01 to 4 molar. Into each test-tube is put a filtered saturated solution of eosin (specific gravity of 1050), in the first eight tubes under the salt solution, and in the last eight tubes on the top of the salt solutions.

Except in the tubes of the very lowest concentrations, penetration by intertraction takes place, and what is specially striking in the experiments is that intertraction occurs with great rapidity—the eosin solution being carried up or down despite the very great differences in specific gravity.

Table III.

Layers.	Diffusion (H_2O superposed on HCl).	Intertraction (2 mol. HCl superposed on 1 mol. NaCl).					Intertraction (1 mol. KNO_3 on 1·4 mol. KCl).
After 24 hours.		After 3 mins.	After 6 mins.	After 1 hour.	After 14 hours.	After 24 hours.	After 6 mins.
1	0	—	—	47·0	22·5	21·5	0·2
2	0	4·4	3·5	4·1	8·25	9·5	0·25
3	0	0·9	1·3	4·05	5·8	7·0	0·3
4	0	0·45	0·75	3·95	7·65	6·6	0·4
5	0	0·45	0·7	3·9	6·8	6·7	0·5
6	1·3	0·3	0·8	4·25	7·4	7·2	0·8
7	18·3	0·35	0·65	3·9	6·8	6·3	3·5
8	2 mol. HCl	0·4	0·9	4·0	6·8	6·4	1·4 mol. KCl
				75·15	71·1	71·9	

The figures indicate the number of cubic centimetres of 1/10 molar sodium hydroxyde necessary to neutralise the hydrochloric acid, and in the case of the KCl–KNO_3 combination 1/10 molar silver nitrate.

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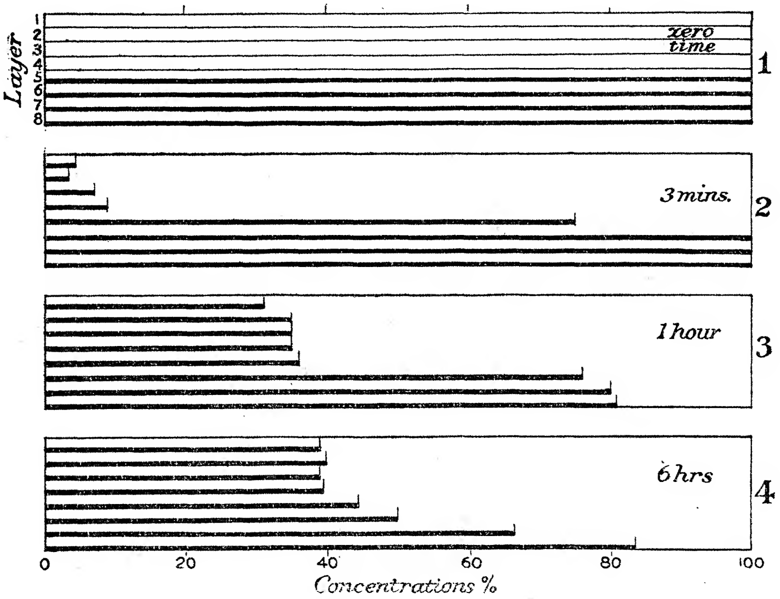
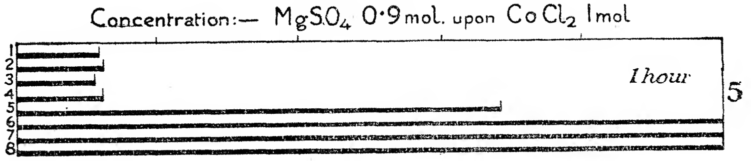
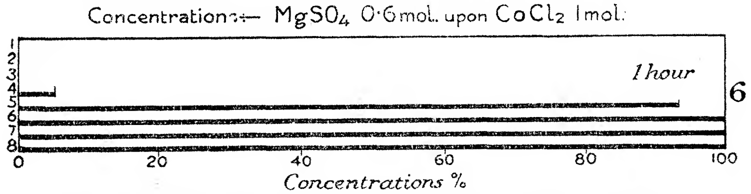
* In this connection I may point out, that the quickened diffusion of hydrochloric acid (in sodium chloride solution) diffusing into sodium chloride solution of the same concentration (as observed first by Arrhenius and studied by Abegg and Rose) and satisfactorily explained by the ionic theory, is *not* the cause in the experiments described above, as the movement of the hydrogen ion in Arrhenius's experiments is only accelerated three and a half times, while the progress of the hydrochloric acid is here ± 2,000 times more rapid than in the ordinary diffusion.

Thus far we have investigated only the rate at which mixing by intertraction occurs. It seemed desirable to get some idea of the amount of the chemical substances transferred from the one intertracting fluid into the other. A few illustrative experiments are given in Table III.

Concentration :—$MgSO_4$ (1 molar) upon $CoCl_2$ (1 mol.).







Length of black lines shows degree of concentration of $CoCl_2$.

For the purposes of the analysis the column of fluid, which was 20 cm. high, was divided into eight sections, about 4 c.c. of fluid being contained in each. In Table III are set forth a series of results which apply to hydrochloric acid diffusing upwards into water (section 1). In the second section we have the results obtained by hydrochloric acid penetrating by intertraction into sodium chloride solution, and in the third potassium chloride penetrating by intertraction into potassium nitrate.

In the diagram are set out a series of results applying to magnesium sulphate superposed on cobalt chloride. It is divided into sections; in the first section (1–4) is depicted the progress of the intertraction, the analysis having been made after three different time-intervals. The lower sections (5 and 6) of the diagram are to be read in relation to No. 3.

In conclusion, I have much pleasure in expressing my thanks to the Committee of the Inoculation Department for the facilities afforded to me for the carrying out of this research, and to Sir Almroth Wright for the interest he has taken in this research and his kind assistance in framing this paper.

The Absorption Spectrum of Potassium Vapour.

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[Plate 5.]

1. *Introductory.*

In connection with the investigation of the vacuum arc spectrum of potassium,* which was undertaken mainly to improve the existing measures, it was found that the type of lamp used in that experiment was unsuitable for the production of the higher members of the series. Already Wood† has shown that the principal series of sodium is much more complete in the absorption than in the emission spectrum, and has extended the series up to $m = 57$. Bevan‡ repeated the experiments with the other alkali elements and was able to extend the principal series in each case very considerably. In view of the importance of obtaining accurate measures of these lines and a possible extension of the series, so that they may afford data which will help to throw some light on the question as to the nature of the formula giving series lines, it was thought desirable to repeat the experiment of Bevan with instruments of greater dispersion. The results which have been accomplished in the repetition of the work may be briefly summarised as follows:—

(1) The number of members of the series has been raised from twenty-four

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* 'Roy. Soc. Proc.,' A, vol. 99, p. 69 (1921).

† R. W. Wood, 'Astrophys. Journ.,' vol. 29, p. 97 (1909); R. W. Wood and R. Fortrat, 'Astrophys. Journ.,' vol. 43, p. 73 (1916).

‡ 'Phil. Mag.,' vol. 19, p. 195 (1910).